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Analysis of the impact of changes in surface water quality on the dynamics of treatment processes in drinking water treatment technological systems

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ABSTRACT

The study presents the results of the analyses of changes in the physicochemical and bacteriological condition of the Dunajec River waters in the years 2012–2021. The physicochemical condition was characterized based on the tests of 16 parameters: pH, specific electrolytic conductivity (SEC), total suspended solids, turbidity, color, dissolved oxygen, five-day biochemical oxygen demand, ammonium ion, nitrates, nitrites, phosphates, sulfates, chlorides, total iron, manganese, phenolic index. The bacteriological condition was assessed by analyzing the indices of coliform bacteria and *Enterococcus faecalis*. The analysis of the physicochemical state of the Dunajec River waters was carried out against the background of changes in water-sewage management, industry, land use, hydrological and meteorological conditions. The average values of physicochemical and bacteriological indicators of the Dunajec River waters tested over the years 2012–2021 were within the A1 and A2 categories of surface water quality. The results of the maximum tests in the year for such parameters as: total suspended solids, color, total iron, pH, ammonium ion, phenolic index, coliform bacteria and *E. faecalis* were in the A3 category of surface water quality. The analyses carried out showed that in the study period a decrease in nitrates, nitrites, sulphates, coliform bacteria and *E. faecalis* was observed as well as the rise of total suspended solids and pH of water. The technology used in the water treatment plant in Stary Sącz allows for an effective removal of physicochemical and bacteriological impurities from the surface water taken for the needs of the plant. The concentrations (annual average and maximum values in the year) of individual quality indicators of the treated water tested over the years 2012–2021 did not show any exceedance of permissible standards.

Keywords: Surface water quality; Water classification, Water treatment processes

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1. Introduction

Water is a unique commodity inherited from generation to generation [1]. The resources of freshwater which is clean and safe for human health have been decreasing and deteriorating year by year due to contamination with solid particles and toxic substances [2]. Therefore, measures should be taken to protect freshwater resources and to improve its quality, which is associated with sustainable environmental and societal development [3]. Growing urbanization leads to increased exploitation of water resources [4]. Agricultural, economic and industrial activities as well as climate changes (floods, droughts, changes in the amplitude of precipitation [5], and thus surface water flows) have a significant impact on the deterioration of the parameters of surface water quality [6].

The monitoring of surface water quality, combined with the assessment of water status, has become a critical and necessary issue in recent years [7], due to concerns about future shortages of freshwater resources [8] and pollutants penetrating them (including newly emerging pollutants such as pharmaceuticals) [9]. Surface waters are particularly exposed to pollution entering them together with household or industrial sewage from unsewered areas and discharge from municipal and industrial sewage treatment plants [10–12]. Particular attention should be paid to the efficiency and optimization of processes taking place in municipal and industrial sewage treatment plants [13] and to proper management of sewage sludge [14]. Seasonal variability of precipitation, surface runoff from arable land and artificial surfaces areas as well as groundwater flows affect river flows and pollutant concentrations [15]. Long-term monitoring of water quality combined with quality assessment may ultimately prevent the deterioration of water environment [16]. Routinely monitored water quality parameters, including physicochemical and bacteriological indicators of water quality, allow to characterize the quality of surface waters and to identify pollutants [17]. Water quality monitoring is also a helpful tool in the protection of aquatic organisms [18] and, above all, in ensuring sustainable management of water resources [19]. Haq et al. [20] studied the Ghizer River Basin (GRB) as one of the Indus River basins that hosts rich mineralization and agrogenic activities. 55 water samples were collected and tested for concentrations of potentially harmful elements (PHE). PHE concentrations (chromium, copper, arsenic, cobalt, nickel, manganese, cadmium, lead and zinc) in water of the GRB were used to calculate the potential of non-cancer risks such as chronic daily intake (CDI), hazard quotient (HQ), and cancer risk (CR) [20]. Geospatial and statistical analyses showed that lithogenic sources contributed higher to PHE contamination in the water of the GRB than the agrogenic sources [20]. Surface water, groundwater and rainwater in Nigeria was monitored by Ighalo et al. [19] and they identified potential sources of pollution. The researchers identified, as the main water pollutants, industrial sewage (18% of research results), hydrogeological factors (25% of research results) and the type of roofs (31%) [19]. The identification of contamination sources is the first step towards taking appropriate action to reduce the formation of pollution in the aquatic environment. The next step is to take corrective action, apply appropriate measures and technologies to reduce the production of pollutants and to improve water and wastewater treatment systems. Belayutham et al. [21] worked on the development and implementation of a construction work schedule aimed at preventing water contamination by pollution generated at construction sites. Chen et al. [22] developed a tool to assess the efficiency of water protection and pollution control technologies at the process level in a cleaner production technology in the textile industry.

The objective of the research work presented here was to analyze changes in the physical, chemical and bacteriological state of the waters of the Dunajec River at the 116,000 km in 2012–2021 against the background of changes in water and wastewater management, industry, land use, hydrological and meteorological conditions in the vicinity of water intake for the agglomeration of Nowy Sącz and Stary Sącz. The analysis was extended by adding selected indicators of the quality of water treated in the water treatment plant (WTP) in Stary Sącz, and on this basis conclusions were formulated whether the technological system used in the WTP in Stary Sącz is adapted to remove pollutants from the waters of the Dunajec River.

2. Materials and methods

The analysis of the physicochemical and bacteriological condition of waters of the Dunajec River was carried out on the basis of the results of water samples taken in the years 2012–2021 by the Accredited Laboratory for Water and Wastewater Testing (Accreditation No. AB 980), belonging to the Water Mains Company Ltd., ("Sądeckie Wodociągi" L.L.C.) in Nowy Sącz. Water samples were collected on the right bank of the river at 116,000 km, that is, at the place of water intake for the WTP in Stary Sącz. The paper presents a detailed analysis of 16 characteristic physical and chemical indicators of water quality: pH, specific electrolytic conductivity, suspended solids, turbidity, color, dissolved oxygen, five-day biochemical oxygen demand (BOD_5), ammonium ion (NH_4), nitrates (NO_3), nitrites (NO_2), phosphates (PO_4), sulfates (SO_4), chlorides (Cl), total iron, manganese, phenol index as well as 2 bacteriological indicators: coliform bacteria and *Enterococcus faecalis*. In total, in the period of 10 y, between 255 and 295 studies were carried out for each of the examined indicators (1 or 2 times a month depending examined indicator). Turbidity was measured by the nephelometric method (PN-EN ISO 7027-1:2016-09), pH by the potentiometric method (PN-EN ISO 10523:2012), electrical conductivity at 25°C by the conductometric method (PN-EN 27888:1999). The color of water was tested in compliance with PN-EN ISO 7887:2012; Ap1:2015-06, BOD_5 in compliance with PN-EN 1899-2:2002. Chlorides, sulphates, phosphates and ammonium ion were tested by ion chromatography (PN-EN ISO 10304-1:2009/AC:2012). Iron and manganese were tested by atomic absorption spectrometry (ASA) with electrothermal atomization (graphite cuvette) PN-EN ISO 15586:2005 and PN-EN ISO 17294-2:2016-11.

Microbiological tests were carried out in an accredited water and sewage testing laboratory, using the plate method (deep culture) and the membrane filtration method, based on the PN-EN ISO 7899-2: 2004 standard for *Enterococcus faecalis* and the PN-EN ISO 9308-1: 2014-12 standard + A1:2017-04 for coliform bacteria.

Samples were collected and analyzed in accordance with the standards and procedures listed for individual quality indicators (materials and methods), so as to obtain the required accuracy and precision of the obtained test results.

Meteorological conditions in the catchment basin were characterized on the basis of own observations and data provided by the Institute of Meteorology and Water Management (IMGW) in Cracow [23]. The hydrological conditions were characterized on the basis of data comprising daily measurements of water levels and flows of the Dunajec River from the water gauge station in Gołkowice, located at 121,080 km of the Dunajec River, in the years 2012–2021. The data was made available by the Institute of Meteorology and Water Management (IMGW) in Cracow [24].

The land use structure of the Dunajec River catchment basin was determined on the basis of the data contained in the study 'Upper Vistula Catchment Basin' [25]. The location of point pollution sources was determined on the basis of data collected from the hydroportal of the IT System for the Protection of the Country (ISOK) [26], on own observations and field inspections.

At the initial stage of the analysis, characteristic concentrations of the analyzed water parameters were determined, that is, minimum, average, maximum values, standard deviations and medians. The results of the tests of the selected indicators were subject to a detailed analysis in terms of the requirements to be met by surface waters used to supply the population with drinking water, set out in Annex 1 to the Regulation of the Minister of Maritime Economy and Inland Navigation of August 29, 2019 [27]. The regulation establishes recommended and acceptable values for physical, chemical and bacteriological indicators and defines three categories of water quality, which, depending on the degree of contamination, must be subjected to standard treatment processes in order to obtain water intended for consumption. The regulation establishes three categories of water quality:

- category A1 – water requiring simple physical treatment, in particular filtration and disinfection;
- category A2 – water requiring typical physical and chemical treatment, in particular, pre-oxidation, coagulation, flocculation, decantation, filtration and disinfection by final chlorination;
- category A3 – water requiring high-efficiency physical and chemical treatment or biological methods, in particular oxidation, coagulation, flocculation, decantation, filtration, adsorption on activated carbon, disinfection by ozonation or final chlorination.

Then, the relationship between the concentrations of water quality parameters and water flow rate was investigated. Subsequently, in order to determine the temporal and seasonal changes of the examined water quality parameters, an analysis of trends was carried out. Next, the selected indicators of the quality of water treated in the WTP in Stary Sącz were analyzed, and on that basis conclusions were formulated whether the technological system used in the WTP in Stary Sącz was adapted to remove pollutants from the waters of the Dunajec River.

3. Study area

The Dunajec River is the largest Carpathian River. It is a right tributary of the Vistula River, flowing through the Orava and Nowy Targ Valley, the Pieniny Mountains, Beskid Sądecki mountain range, the Nowy Sącz Valley, the Rożnów Foothills and the Vistula Lowland. It has been created through the connection of the Biały Dunajec River and Czarny Dunajec River near Nowy Targ. Hydrographically, it is a part of the Upper Vistula water basin. The length of the river, including the Czarny Dunajec, is 247 km. The catchment area is 6,804 km^2 (4,852 km^2 in Poland) [28].

In the upper part of the catchment there are the cities of Zakopane and Nowy Targ. The Czorsztyn-Niedzica reservoir, completed in July 1997, together with the reservoir in Sromowce Wyżne, completed a few years earlier, greatly influence the conditions of river water management, leveling the flows and retaining a significant part of dragged and floating solids. In the further part of the Dunajec River, there are the towns of Szczawnica and Krościenko, and then the city of Stary Sącz. The Czorsztyn-Niedzica and Sromowce Wyżne reservoirs have a significant impact on the characteristics of flows in the middle course of the Dunajec, and thus also on the operation of surface and infiltration intakes located in the immediate vicinity of this river.

The Dunajec flows through areas used mainly as agricultural areas, to a lesser extent as recreational areas. In these areas, there are also small production plants of building materials and agri-food products. The land use structure of the Dunajec catchment basin, according to the data provided in the study 'Upper Vistula Catchment Basin' [25], is quite diverse. The share of arable land is 37%, orchards 2.5%, grassland and pastures 13.4%. In total, the share of agricultural land is 52.9% and that of forests – 37.8%. Along the section from the Czorsztyn – Niedzica and Sromowce Wyżne reservoirs to the intake area in the towns of Stary Sącz and Podegrodzie, the Dunajec River takes the tributaries of such watercourses as, for example, Grajcarek, Krośnica, Obidzki Stream, Kamienica, Czarna Woda, Jaworzynka, Jarząbka and Słomka.

The graphic form of the course of the catchment boundaries for the analyzed cross-section at the water intake site is shown in Fig. 1.

The main source of pollution in the Dunajec River basin was attributed to treated sewage from municipal sewage treatment plants and surface runoff from agricultural fields. Until 2018, the catchment area of the Dunajec River above the water intake was not sewered. In the analyzed area, 69 sites of the discharge of sewage, rainwater, meltwater, medicinal and technological waters into surface waters were identified, including: household and municipal sewage (32 sites), industrial wastewater (3 sites), rainwater and snowmelt (32 sites) drainage waters (1 site), medicinal waters (4 sites) and technological sewage (4 sites) [26].

The site of the intake of surface water from the Dunajec River belongs to the Nowy Sącz poviat, where the natural landscape is dominated by the Carpathian flysch [29]. Geomorphological conditions influence a significant share of groundwater flows and surface runoff towards the river valley, in compliance with the slopes of the terrain. The average annual precipitation in the discussed area is 700–800 mm

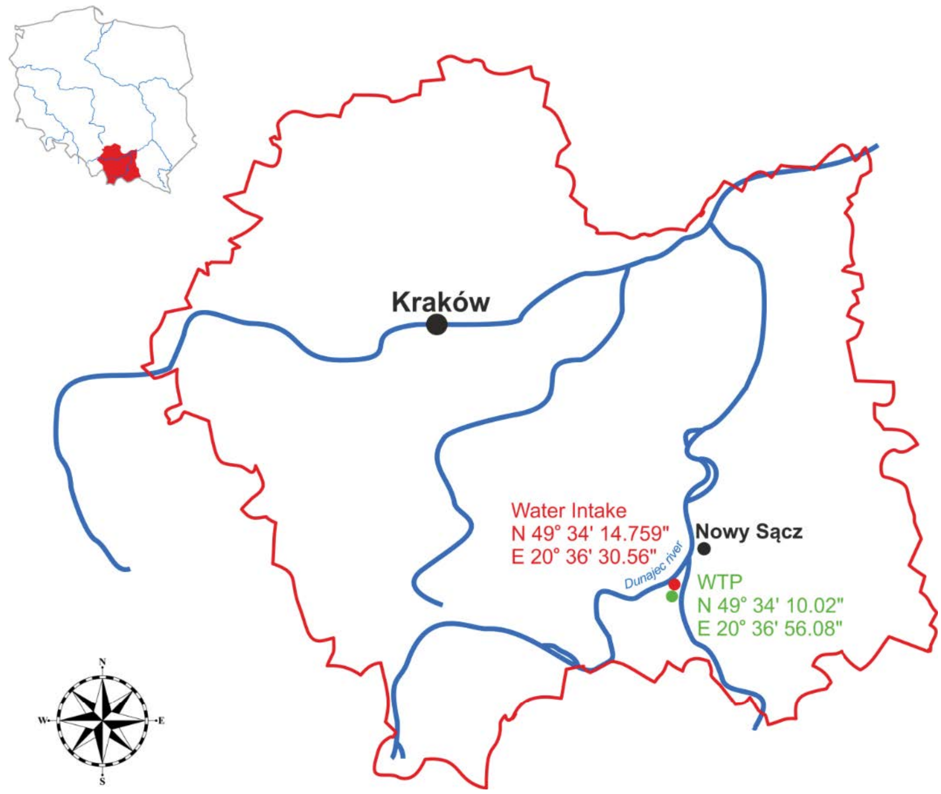

Fig. 1. Location of water sampling site from the Dunajec River for the cross-section at the water intake.

with the predominance of summer precipitation (> 500 mm) over winter precipitation (250–300 mm). And the average share of solid precipitation in the total amount of precipitation is 20%. The occurrence of torrential summer precipitation increases the risk of flood [30]. Watercourses are characterized by spring floods and summer floods (rain-snow regime). The average unit runoffs are assessed as high and they amount to 10–40 $L \cdot s \cdot km^{-2}$, and the amount of precipitation and surface runoff determine flows in watercourses. The area of the Stary Sącz municipality is characterized by water resources with a significant disproportion in time and space, frequent changes of water levels, even during the day, and a significant flooding potential. In the analyzed yearslong period, the flows of the Dunajec River at the water gauge station in Gołkowice ranged from NNQ = 6.800 $m^3 \cdot s^{-1}$ to WWQ = 894.000 $m^3 \cdot s^{-1}$. The average annual flow in the analyzed period was SSQ = 42.040 $m^3 \cdot s^{-1}$, while the inviolable flow SNQ = 5.333 $m^3 \cdot s^{-1}$ [30].

4. Results and discussion

The analysis of the water quality of the Dunajec River in the analyzed period showed that the oxygen conditions of the river are diverse and change with the seasons. The dissolved oxygen concentration in the water ranged from 7.4 to 14.8 $mg \cdot O_2 \cdot dm^{-3}$. The concentration of dissolved oxygen in water ranged from 7.4 to 14.8 $mg \cdot O_2 \cdot dm^{-3}$. Water temperature directly affects the life cycle of aquatic organisms and their metabolism, as well as the processes of photosynthesis, which occur much faster at higher temperatures [31]. Therefore, oxygen is taken up from water by organisms to a greater extent in spring and summer (Table 1). Biodegradable organic materials such as proteins, carbohydrates and fats may enter surface waters with sewage. In the examined years, the five-day biochemical oxygen demand (BOD_5 = 0.0 – 5.0 $mg \cdot O_2 \cdot dm^{-3}$) exceeds the criterion of good ecological status. Large amounts of biodegradable matter are dangerous to the aquatic environment because microorganisms initiate biochemical reactions, using oxygen dissolved in water to decompose waste and reducing its content in the water reservoir. Increased BOD_5 values were observed in the months of late autumn and winter (IX-III), when biochemical transformation processes occur slower due to low temperature and reduced growth of microorganisms. BOD_5 concentrations decrease in the summer period (IV-X) due to the increase in biochemical transformations [32] (Table 1). Similarity of the spring-summer-autumn-winter relationships was observed for ammonium ion, nitrates and nitrites (Table 1). The concentrations of nitrates (from 0.9 to 8.9 $mg \cdot NO_3 \cdot dm^{-3}$) and nitrites (from 0.002 to 0.107 $mg \cdot NO_2 \cdot dm^{-3}$) were at an average level, and those of ammonium ion (from 0.00 to 1.29 $mg \cdot NH_4 \cdot dm^{-3}$, on average 0.053 $mg \cdot NH_4 \cdot dm^{-3}$) at a low level with the exception of a single annual peak of 1.29 $mg \cdot NH_4 \cdot dm^{-3}$. The changes in the concentrations of nitrates, nitrites and ammonium ion are subject to slight fluctuations, which is related to seasonal changes, including changes in water temperature, water levels and the biological life cycle (Table 1).

The waters of the Dunajec River were characterized by a natural, slightly alkaline reaction with pH from 7.6 to 8.5.

Table 1
Monthly selected water quality indicators of the Dunajec River (part 1)

Months	Dissolved oxygen			BOD_5			Ammonium ion			Nitrates			Nitrites		
	$mg·O_2·dm^{-3}$			$mg·O_2·dm^{-3}$			$mg·NH_4·dm^{-3}$			$mg·NO_3·dm^{-3}$			$mg·NO_2·dm^{-3}$		
XI	9.7	11.4	13.7	1	2	5	0.01	0.05	0.14	1.7	3.5	4.8	0.004	0.026	0.055
		3.6–1.0			2.0–0.7			0.05–0.03			3.71–0.79			0.024–0.013	
XII	9.3	12.1	13.7	0	2	3	0.01	0.06	0.27	2.75	3.8	4.9	0.009	0.024	0.065
	5.7–1.6			2.0–0.8			0.04–0.06			3.77–0.67			0.018–0.014		
I	11.0	12.9	14.8	1	3	4	0.01	0.10	0.18	3.6	4.9	7.8	0.005	0.019	0.054
		8.1–1.1			3.0–0.7			0.04–0.05			4.69–0.95			0.017–0.011	
II	11.0	12.6	13.6	1	3	4	0.02	0.07	0.15	4.3	5.4	6.7	0.011	0.024	0.075
		10.4–1.4			2.5–0.7			0.05–0.04			5.30–0.73			0.019–0.016	
III	10.0	11.9	13.7	2	3	4	0.02	0.05	0.18	4.2	5.8	8.9	0.003	0.023	0.041
		13.3–1.3			2.0–0.6			0.04–0.03			5.38–1.29			0.021–0.010	
IV	8.3	11	13.5	2	2	3	0.02	0.06	0.11	3.5	5.0	7.6	0.010	0.032	0.101
		1.0–0.6			2.0–0.5			0.05–0.03			4.87–0.89			0.028–0.017	
V	8.9	10.6	12.5	0	2	3	0.00	0.04	0.14	3.3	4.3	6.7	0.015	0.039	0.115
		1.9–0.5			2.0–0.6			0.04–0.03			4.18–0.76			0.037–0.019	
VI	8.0	9.3	12.7	1	1	2	0.00	0.04	0.14	1.7	3.5	5.5	0.010	0.032	0.055
		3.0–0.9			1.0–0.5			0.03–0.03			3.50–0.90			0.030–0.012	
VII	7.9	9.4	10.4	1	1	2	0.00	0.05	0.13	1.3	2.9	4.2	0.014	0.037	0.060
		9.5–0.7			1.0–0.5			0.04–0.04			2.68–0.88			0.036–0.015	
VIII	7.5	9.0	11.5	1	1	3	0.00	0.08	1.29	0.95	2.8	5.9	0.006	0.027	0.059
		9.05–1.0			1.0–0.6			0.03–0.25			2.60–1.13			0.026–0.013	
IX	7.4	9.1	10.3	0	1	3	0.00	0.05	0.15	0.9	2.8	4.8	0.002	0.030	0.107
		9.4–0.74			1.0–0.7			0.04–0.04			2.88–0.94			0.025–0.023	
X	8.1	10.2	13.1	1	1	2	0.00	0.03	0.07	1.39	2.9	4.0	0.006	0.020	0.051
		2.5–1.3			1.0–0.5			0.03–0.02			2.77–0.71			0.019–0.008	

Phosphate concentration in the analyzed period ranged from 0.000 $mg·dm^{-3}$ to 0.366 $mg·PO_4·dm^{-3}$ with an average value of 0.049 $mg·PO_4·dm^{-3}$. The concentration of chlorides varied from 4 to 16 $mg·Cl·dm^{-3}$. The sulphate concentration ranged from 9.0 to 35.8 $mg·SO_4·dm^{-3}$ with an average value of 20.5 $mg·SO_4·dm^{-3}$ (Table 2).

The observed changes in the concentrations of chlorides, sulphates and specific electrolytic conductivity (SEC in the range from 241 to 515 $\mu S·cm^{-1}$, on average 329.6 $\mu S·cm^{-1}$) (Table 2), can be attributed, among others, to the discharge of salts into waters, for example, sodium and potassium chlorides in the winter period (from December to February), resulting from winter maintenance of roads, as well as from the drainage of medicinal waters (chlorides, sulphates). They are also caused by non-uniform flows and changes in water levels in the river.

The physical, chemical and bacteriological condition of waters of the Dunajec River in 2012–2021 was assessed on the basis of the Regulation of the Minister of Maritime Economy and Inland Navigation of August 29, 2019 on the requirements to be met by surface waters used to supply the population with water intended for human consumption [27]. The concentration values obtained in the tests were compared with the limit values specified in the standards for a given water quality class, and quality classes for the waters of the Dunajec River were determined.

In terms of dissolved oxygen, SEC, chlorides, sulfates, phosphates and nitrates, the waters of the Dunajec River were classified as A1 (in 100% of the collected samples) (Fig. 2). The standards of water category A2 involved the content of *E. faecalis* bacteria in 88.4% (for the standard of 1,000 cfu in 100 mL) of the collected water samples, the phenol index in 90.1% of the samples (up to the standard value <0.0050 $mg·dm^{-3}$ (Fig. 3), color (in 11.5% of the collected values of water samples were from 20 to 100 $mg·Pt·dm^{-3}$), coliform bacteria (up to 5,000 cfu in 100 mL in 5.2% of the samples), BOD_5 for the standard from 3 to <5 $mg·O_2·dm^{-3}$ (in 1.25% of the samples), pH within the range of 5.5–9.0 (in 0.3% of the samples), ammonium ion (in 0.3% of the samples) and total iron (0.3% of the collected samples for the standard from 0.3 to 2.0 $mg·Fe·dm^{-3}$) (Fig. 2), while the above-standard parameters of total suspension exceeding the standard of 35 $mg·dm^{-3}$ (Fig. 4) in 8.1% of the tested samples (Fig. 2), coli bacteria in 0.8% of the samples (standard of 50.000 cfu in 100 mL) and *E. faecalis* in 2.7% (for the standard of 10,000 cfu in 100 mL) of the tested samples were decisive to classify the waters of the Dunajec River to category A3 (Fig. 5).

Pejman et al. studied spatial and seasonal changes in water quality in the Haraz Basin [33]. For this purpose, they used a multivariate statistical technique, that is, cluster analysis and factor analysis. The researchers analyzed water samples collected at 8 sites in the river during four seasons

Table 2
Monthly selected water quality indicators of the Dunajec River (part 2)

Months	Phosphates			Chlorides			Sulfur			pH		SEC		
	$mg·PO_4·dm^{-3}$			$mg·Cl·dm^{-3}$			$mg·SO_4·dm^{-3}$			–		$\mu S·cm^{-1}$		
XI	0.000	0.050	0.140	6.0	8.6	12.0	13.0	21.6	35.8	7.9	8.5	283	326	358
	0.038–0.032			8.50–1.78			21.3–4.5			8.1–0.1		328–15.8		
XII	0.000	0.031	0.060	7.0	9.9	12.0	13.6	20.9	27.2	7.6	8.4	304	344	414
	0.031–0.017			10.0–1.61			20.9–3.7			8.1–0.2		338–23.9		
I	0.000	0.045	0.170	6.0	10.4	14.0	14.9	20.6	24.4	7.9	8.3	300	366	515
	0.027–0.047			11.0–1.85			20.2–3.0			8.1–0.1		355.5–49.7		
II	0.01	0.056	0.200	9.0	12.5	16.0	13.0	22.7	27.0	7.7	8.3	323	376	492
	0.033–0.056			12.0–1.71			22.8–3.3			8.1–0.1		368–44.2		
III	0.000	0.033	0.150	6.0	10.6	14.0	14.4	23.0	28.7	7.8	8.3	293	341	383
	0.024–0.030			11.0–2.17			23.4–3.3			8.1–0.1		342–23.7		
IV	0.000	0.052	0.270	8.0	11.0	14.0	18.3	22.1	27.9	8.1	8.4	283	332	388
	0.037–0.054			10.50–1.87			22.3–2.3			8.2–0.1		327.5–26.1		
V	0.000	0.046	0.366	6.0	10.2	14.0	14.5	21.7	29.3	7.9	8.3	241	319	367
	0.022–0.073			10.0–1.96			22.1–3.0			8.1–0.1		323.5–25.2		
VI	0.000	0.046	0.160	4.0	8.2	14.0	11.4	18.3	29.1	7.7	8.3	256	314	427
	0.036–0.040			8.0–1.94			18.3–3.4			8.1–0.1		301–38.9		
VII	0.01	0.061	0.210	5.0	7.7	11.0	11.9	19.8	29.1	7.9	8.4	271	311	427
	0.046–0.051			8.0–1.26			19.7–3.1			8.2–0.1		300–39.9		
VIII	0.000	0.062	0.258	4.0	7.9	10.0	14.5	18.3	21.5	7.9	8.7	256	311	378
	0.037–0.070			8.0–1.49			17.9–1.9			8.1–0.2		307–26.3		
IX	0.009	0.057	0.180	4.0	8.8	10.0	12.0	18.4	23.9	7.7	8.5	287	321	393
	0.046–0.043			8.0–1.50			18.3–3.2			8.2–0.2		317–24.5		
X	0.010	0.040	0.193	5.0	8.6	11.0	9.0	19.3	24.6	7.9	8.4	269	322	356
	0.029–0.037			10.0–1.615			19.3–3.3			8.1–0.1		321–17.1		

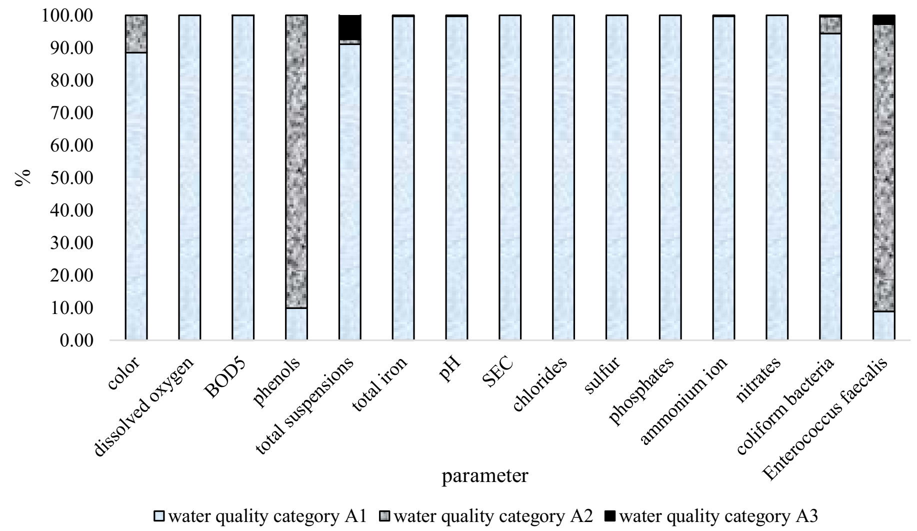

Fig. 2. Percentage of selected physical and chemical parameters in the particular classes of surface water quality.

(summer and autumn 2007, winter and spring 2008). Ten water quality parameters were taken into account, that is, dissolved oxygen, coliform bacteria, pH, water temperature, biochemical oxygen demand, nitrates, phosphates, turbidity, content of solids and flow. The basic analysis of the factors helped single out and identify the sources responsible for the changes in water quality in four seasons. Temperature and flow, total content of solids and nitrates were the most important parameters affecting the changes in water quality in all year seasons [31].

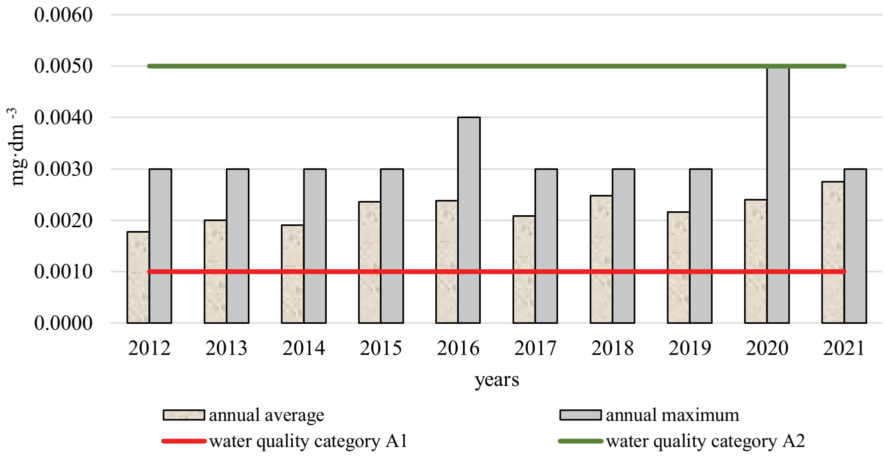

Fig. 3. Variable content of the phenolic index in the waters of the Dunajec River.

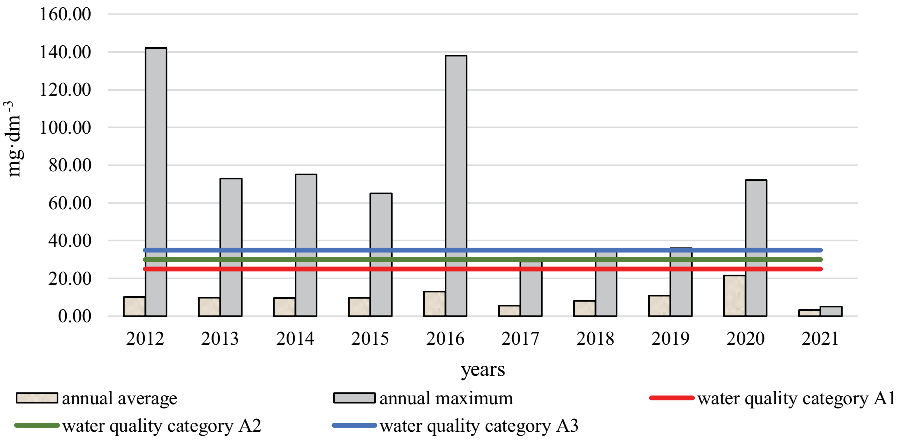

Fig. 4. Variable content of total suspensions in the waters of the Dunajec River.

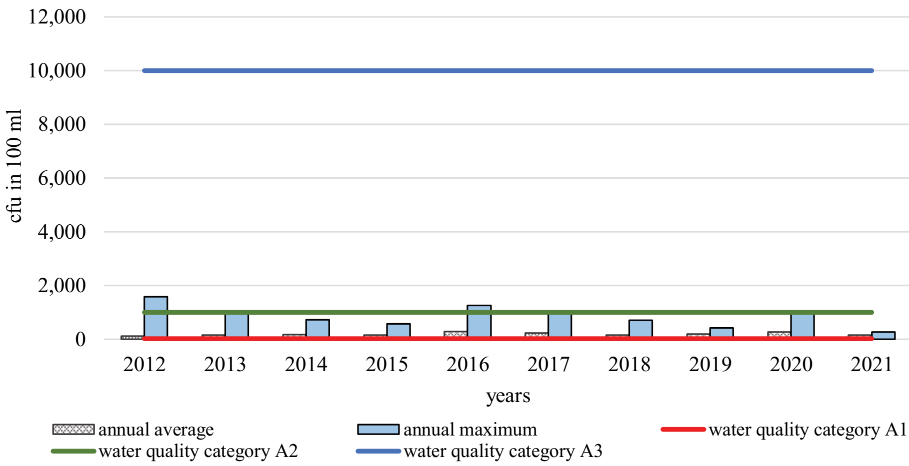

Fig. 5. Variable content of *Enterococcus faecalis* in the waters of the Dunajec River.

The future impact of urban land use and climate change on surface water quality in the Des Plaines River catchment in the state of Illinois in 2010–2030 was investigated and predicted by Wolson and Weng [34]. The researchers found that climate change would have a greater impact on water quality than land use change in the catchment of the Des Plaines River, and the concentrations of total suspended solids would be higher in winter than in summer. It was also found that seasonal variability of phosphorus concentration depends on climate change, and that large open space reduces phosphorus concentration [34].

In turn, the analysis of spatial and seasonal changes in water quality parameters in the Keban Dam Reservoir in Turkey and the identification of the main factors and sources of pollution affecting water quality in the reservoir using multidimensional statistical techniques were studied by Varol [2]. Ali and Muhammad [35] assessed the water quality in the Astore River in the western Himalayas in northern Pakistan in terms of 17 physicochemical parameters of suitability for domestic, drinking and irrigation purposes. Results indicated that turbidity, fluoride, and nitrate (NO_3) values surpassed the safe limits in 60%, 2.5%, and 2.5% of samples [33]. Water quality index (WQI) revealed that only 19.5% of samples were classified in poor and very poor water quality classes due to turbidity and NO_3. Irrigation and corrosion indices of the river showed its suitability for agriculture and corrosive tendency [33].

Hydrometeorological conditions, apart from the inflow of pollutants to the river, were the key factor having a direct impact on the changes in the concentrations of the tested water quality indicators of the Dunajec River (Table 3). Along with the analyzed flows, the following factors had positive correlation: color, turbidity, total suspension (Fig. 6), total iron, nitrites and *E. faecalis*, while pH (Fig. 7), SEC and chlorides were negatively correlated. Also a positive correlation was obtained between other parameters, for example, turbidity and color, total suspensions, total iron, manganese, SEC, chlorides and phosphates (Table 3).

In the last 3 y of research (2019–2021), the reductions of BOD_5, sulphates, nitrates and nitrites, coliform bacteria and *E. faecalis* were observed. In the last 4 y, the area upstream of the water intake from the Dunajec River was sewered, which could have had a positive impact on the improvement of water quality indicators in the area of the intake.

A rising trend was observed for total suspensions, chlorides, pH and phosphates in the last 2 y of the research. The years 2020 and 2021 were characterized by hydrological drought, which could have resulted in lower water levels and lower flows, and thus an increase in pH, phosphates and chlorides.

It should be noted that the technological system used in the WTP in Stary Sącz is adapted to treat surface waters with the equipment category A2 and A3. The system uses: volumetric coagulation combined with sedimentation in vertical settling tanks, filtration on rapid filters with a bed of quartz sand with contact coagulation, indirect oxidation with ozone, filtration on filters with a bed of granulated activated carbon and final disinfection using UV radiators and chlorine gas [36]. Applied water treatment technology allows for the effective removal of physicochemical impurities

Table 3
Correlation of selected parameters of water quality and flow rate of the Dunajec River

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1		–0.18	0.04	0.10	0.48	0.56	0.52	0.17	0.04	–0.38	–0.27	0.43	–0.14	0.20	–0.06	0.44	0.22	0.35	0.27
2	–0.18		0.55	0.12	–0.07	–0.12	–0.11	–0.22	0.19	0.38	0.37	–0.07	0.29	–0.04	0.52	–0.13	0.23	0.08	–0.02
3	0.04	0.55		0.07	0.15	0.18	0.15	–0.05	0.05	0.27	0.34	0.05	0.35	0.20	0.47	0.13	0.20	0.15	0.01
4	0.10	0.12	0.07		0.04	0.02	0.02	0.04	0.04	0.05	0.00	–0.05	–0.09	–0.01	–0.05	0.07	0.13	0.11	–0.06
5	0.48	–0.07	0.15	0.04		0.64	0.88	0.25	–0.12	–0.29	–0.25	0.37	0.03	0.08	0.06	0.61	0.24	0.52	0.37
6	0.56	–0.12	0.18	0.02	0.64		0.66	0.26	–0.07	–0.29	–0.16	0.34	0.01	0.06	0.09	0.44	0.21	0.50	0.32
7	0.52	–0.11	0.15	0.02	0.88	0.66		0.31	–0.10	–0.30	–0.26	0.35	0.03	0.12	0.07	0.56	0.31	0.54	0.39
8	0.17	–0.22	–0.05	0.04	0.25	0.26	0.31		–0.05	–0.19	–0.07	0.11	–0.05	0.11	–0.05	0.21	0.03	0.09	0.16
9	0.04	0.19	0.05	0.04	–0.12	–0.07	–0.10	–0.05		–0.15	0.05	–0.01	–0.09	0.00	–0.06	–0.04	–0.04	–0.12	–0.26
10	–0.38	0.38	0.27	0.05	–0.29	–0.29	–0.30	–0.19	–0.15		0.54	–0.26	0.23	–0.13	0.25	–0.38	–0.05	–0.19	–0.32
11	–0.27	0.37	0.34	0.00	–0.25	–0.16	–0.26	–0.07	0.05	0.54		–0.15	0.28	0.03	0.33	–0.26	–0.01	–0.14	–0.28
12	0.43	–0.07	0.05	–0.05	0.37	0.34	0.35	0.11	–0.01	–0.26	–0.15		–0.05	0.30	0.01	0.36	0.19	0.22	0.20
13	–0.14	0.29	0.35	–0.09	0.03	0.01	0.03	–0.05	–0.09	0.23	0.28	–0.05		–0.02	0.33	0.36	0.10	–0.03	–0.15
14	0.20	–0.04	0.20	–0.01	0.08	0.06	0.12	0.11	0.00	–0.13	0.03	0.30	–0.02		0.05	0.06	0.01	0.00	0.08
15	–0.06	0.52	0.47	–0.05	0.06	0.09	0.07	–0.05	–0.06	0.25	0.33	0.01	0.33	0.05		0.04	0.19	0.06	0.19
16	0.44	–0.13	0.13	0.07	0.61	0.44	0.56	0.21	–0.04	–0.38	–0.26	0.36	0.05	0.06	0.04		0.25	0.32	0.33
17	0.22	0.23	0.20	0.13	0.24	0.21	0.31	0.03	–0.04	–0.05	–0.01	0.19	0.10	0.01	0.19	0.25		0.63	0.02
18	0.35	0.08	0.15	0.11	0.52	0.50	0.54	0.09	–0.12	–0.19	–0.14	0.22	–0.03	0.00	0.06	0.32	0.63		0.25
19	0.27	–0.02	0.01	–0.06	0.37	0.32	0.39	0.16	–0.26	–0.32	–0.28	0.20	–0.15	0.08	0.19	0.33	0.02	0.25	

1-Color; 2-Dissolved oxygen; 3-Phenols; 4-BOD_5; 5-Turbidity; 6-Total suspensions; 7-Total iron; 8-Manganese; 9-pH; 10-SEC; 11-Chlorides; 12-Phosphates; 13-Sulfur; 14-Ammonium ion; 15-Nitrates; 16-Nitrites; 17-*Coliform* bacteria; 18-*Enterococcus faecalis*; 19-Flow.

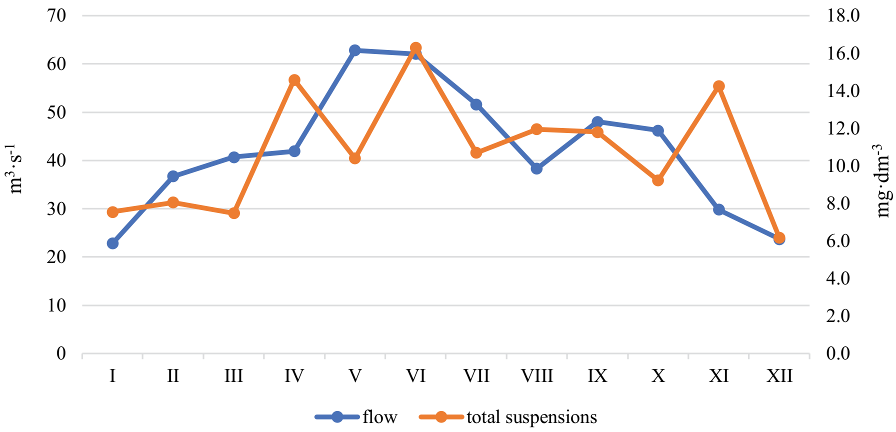

Fig. 6. Seasonal variation of total suspension against the background of monthly flow in the Dunajec River in the years 2012–2021.

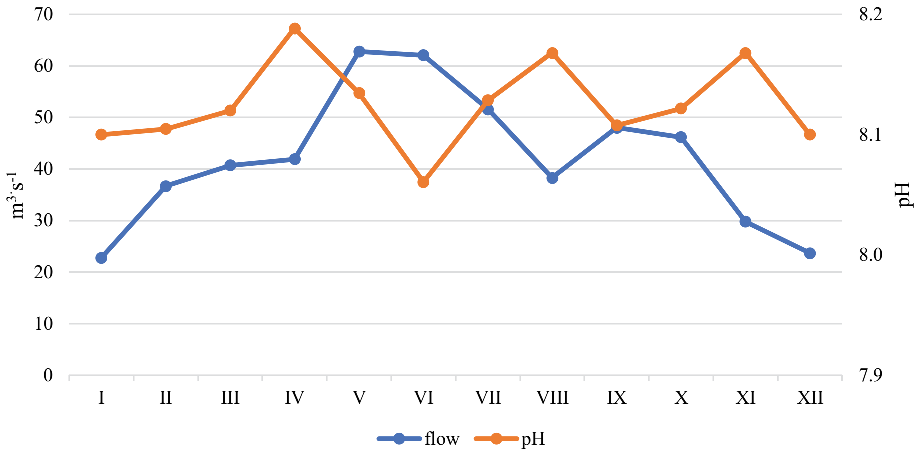

Fig. 7. Seasonal variation of pH against the background of monthly flow in the Dunajec River in the years 2012–2021.

Table 4
Selected physical. chemical and bacteriological indicators of treated water in WTP in Stary Sącz (2012–2021)

	$mg \cdot Pt\ dm^{-3}$	NTU	$mg \cdot Fe\ dm^{-3}$	Coliform (cfu)	*Enterococcus faecalis* (cfu)	$mg \cdot Cl\ dm^{-3}$	$mg \cdot PO_4\ dm^{-3}$	$mg \cdot SO_4\ dm^{-3}$	$mg \cdot NH_4^+\ dm^{-3}$	$mg \cdot NO_3\ dm^{-3}$	$mg \cdot NO_2\ dm^{-3}$
min	0	0.06	0.000	0	0	11	0.000	14.5	0.000	4.4	0.0000
av.	<5	0.11	0.006	0	0	14	0.006	21.4	0.009	8.6	0.0011
max	5	0.36	0.057	0	0	19	0.037	29.3	0.080	14.8	0.0134
SD	0	0.04	0.021	0	0	2	0.008	3.3	0.011	1.7	0.0021
ME	5	0.10	0.004	0	0	14	0.004	21.5	0.006	8.2	0.0004

min - minimum; av. - average; max - maximum; SD - standard deviation; ME - median.

from water, including compounds of inorganic and organic nature, as well as bacteriological impurities [37]. The concentrations (annual average and maximum values in a year) of individual treated water quality indicators tested over the years 2012–2021 were compared with the water quality standards specified in the Regulation of the Minister of Health of December 7, 2017 [38] on the quality of water intended for human consumption (Table 4).

The results of physicochemical and bacteriological analyses of the treated water from the Treatment Plant in Stary Sącz demonstrated that each time the treated water met the requirements for the quality of water intended for human consumption, specified in the Regulation of the Minister of Health [38], and the periodically increased values of physicochemical and bacteriological parameters, among others during a flood or hydrological drought, did not affect the quality of water after treatment processes.

The effectiveness of the technological system in removing selected physical and chemical parameters is illustrated in Fig. 8 for manganese and in Fig. 9 for *E. faecalis*.

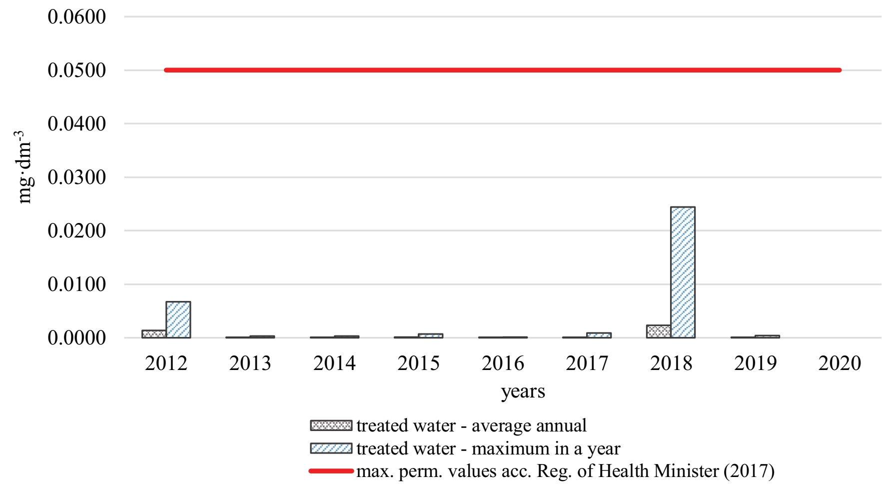

Fig. 8. Results of manganese concentration tests after the water treatment process against the permissible standard.

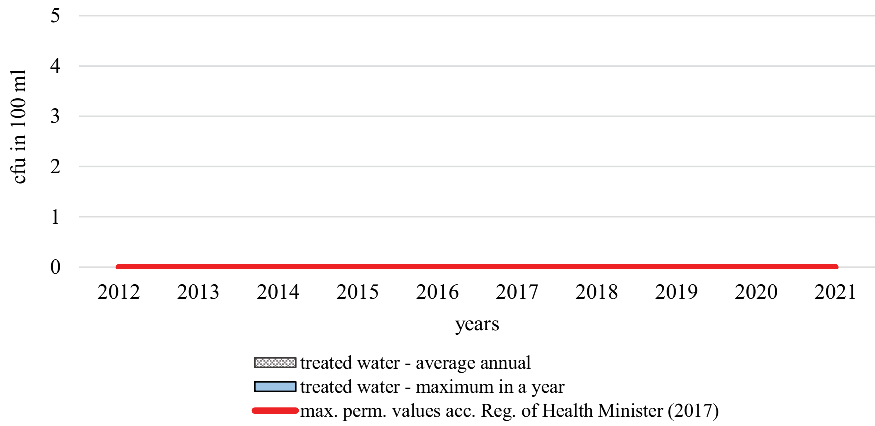

Fig. 9. Results of *Enterococcus faecalis* bacteria after the water treatment process against the acceptable standard.

5. Conclusions

The results of water quality tests of the Dunajec River indicate that the average values of the physicochemical and bacteriological indicators tested over the years 2012–2021 are maintained within the A1 and A2 quality categories. Single results of maximum tests in a year for such parameters as: total suspended solids, phenolic index, coliform bacteria and *E. faecalis* reached the values corresponding to the A3 category of surface water quality, thus being qualified for high-efficiency physical and chemical treatment or for biological methods, in particular oxidation, coagulation flocculation, decantation, filtration, adsorption on activated carbon, disinfection by ozonation or final chlorination.

In terms of dissolved oxygen, SEC, chlorides, sulfates, phosphates and nitrates, the waters of the Dunajec River were classified as A1 (in 100% of the collected samples). The standards of water category A2 involved the content of *E. faecalis* bacteria in 88.4% (for the standard of 1,000 cfu in 100 mL) of the collected water samples, the phenol index in 90.1% of the samples (up to the standard value <0.0050 mg·dm^{-3}, color (in 11.5% of the collected values of water samples were from 20 to 100 mg·Pt·dm^{-3}), coliform bacteria (up to 5,000 cfu in 100 mL in 5.2% of the samples), BOD_5 for the standard from 3 to <5 mg·O_2·dm^{-3} (in 1.25% of the samples), pH within the range of 5.5–9.0 (in 0.3% of the samples), ammonium ion (in 0.3% of the samples) and total iron (0.3% of the collected samples for the standard from 0.3 to 2.0 mg·Fe·dm^{-3}), while the above-standard parameters of total suspension exceeding the standard of 35 mg·dm^{-3} in 8.1% of the tested samples, coli bacteria in 0.8% of the samples (standard of 50.000 cfu in 100 mL) and *E. faecalis* in 2.7% (for the standard of 10,000 cfu in 100 mL) of the tested samples were decisive to classify the waters of the Dunajec River to category A3.

The technological system used in the WTP in Stary Sącz meets the requirements for water treatment of equipment categories A1, A2 and A3, through volumetric coagulation combined with sedimentation in primary settling tanks, filtration on rapid filters with a bed of quartz sand with contact coagulation, indirect oxidation with ozone, filtration on a bed of granulated activated carbon and final disinfection using UV radiators and chlorine gas.

In the years 2019–2021, a decrease in the concentrations of the following indicators in the waters of the Dunajec River was observed: BOD_5, sulphates, nitrates and nitrites, coliform bacteria and *E. faecalis*, which could have been directly affected by the sanitary sewage system installed in 2018–2019.

Hydrometeorological conditions are factors that have a direct impact on the changes in the concentrations of water quality indicators of the Dunajec River. The following were positively correlated with the analyzed flows: color, turbidity, total suspended solids, total iron, nitrites and *E. faecalis*, while pH, SEC and chlorides were negatively correlated.

The water treatment technology used in the Treatment Plant in Stary Sącz allows for an effective removal of physicochemical and bacteriological impurities from the water. The concentrations (annual average and maximum values in a year) of individual treated water quality indicators tested over the years 2012–2021 each time met water quality standards set out in the Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption [38].

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